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12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A large process-zone Bernex 2000 CVD reactor was donated by DuPont to Clemson University in 1995. Due to lack of funds, the reactor was not activated until Fall 1998. Initial runs of the reactor indicated major problems with the pumping system, graphite furnace and the gas/vapor supply systems. Through this project, funds were obtained to repair the reactor and upgrade it for CVD processing of functionally graded coatings and CVI processing of ceramic/ceramic composites. The project was initiated on March 31, 1999.

The proposed upgrade of Bernex 2000 has been completed. The pumping system has been completely redone and a new Liquid Ring Vacuum pump installed. New heating elements have been installed in the furnace and the furnace insulation repaired. Two new peristaltic pumps for metering $SiCl_4$ and $TiCl_4$ liquid precursors have been purchased, installed and wired to the control system. A smaller process-zone graphite furmace has been purchased and interfaced with Bernex 2000.

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Standard Form 298 (Rev.2-89)
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Enclosure 1

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Ecnlosure 2

Table of Contents

List of Appendices

Statement of the Problem Studied

A large process-zone Bernex 2000 CVD reactor was donated by DuPont to Clemson University in 1995. Due to lack of funds, the reactor was not installed until June 1998 using the funds (around $25,000) provided to the P.I. by the Department of Mechanical Engineering at Clemson University. Bernex 2000 is a unique piece of equipment which, due to its unusually large process zone (6 inch diameter by 20 inch height, allows coating and infiltration of real-size parts in addition to test specimens. The estimated value of the equipment is $300,000. The initial runs made using Bernex 2000 indicated that the pumping system, consisting of a Liquid Ring Vacuum pump, a nitrogen ejector, and a Roots Blower Booster pump have been seriously worn out by the prior use and need to be replaced. A similar finding was reached for seven Mass Flow Controllers and for two Metering pumps which dispense liquid precursors, such as $SiCl_4$, $TiCl_4$, etc. Should these worn out components be replaced, the CVD system would be put in the condition which would ensure a high quality of the deposited materials. Through this project, funds were obtained to repair the reactor and upgrade Bernex 2000 for CVD processing of functionally graded coatings and CVI processing of ceramic/ceramic composites. These materials have been studied as a part of the ongoing research under the DEPSCOR project, contract number DAAH04-96-1-0197. The quality of the coatings is greatly affected by the ability of the Chemical Vapor Deposition (CVD) reactor to maintain the desired processing pressure and its ability to provide a strict control of the flow of reactive and carrier gases during a CVD run.

Summary of Most Important Results

The following upgrades of the Bernex 2000 CVD reactor have been completed.

1. **Piping and manifolds for the pumping system has been completely redone.**
2. **A new Nash Liquid Ring Vacuum pump purchased and installed.**
3. **New graphite heating elements have been installed in the furnace.**
4. **The furnace insulation has been repaired.**
5. **Two new Ismatech peristaltic pumps for metering $TiCl_4$ and $SiCl_4$ liquid precursors have been purchased, installed and wired to the control system.**
6. **A new smaller size carbon furnace (Centorr Model 10-2-4x6-G-G-0000-20) has been purchased and connected to the controlled system.**

Selected pictures showing the Bernex 2000 CVD reactor are given in Appendix A.

The process parameters for CVD processing of diamond and TiN coatings using Bernex 2000 have been determined using our multi-length scale modeling of the chemical vapor deposition process which combines the reactor scale, the grain-size scale and the atomistic scale. This modeling effort combines various approaches from the disciplines of reactive-gas fluid dynamics and heat transfer, gas and surface chemical thermodynamics and kinetics, van-der Drift-type modeling of microstructure evolution and kinetic Monte Carlo atomistic-scale deposition modeling techniques. The approach allows determination of the relationship between the process parameter and the microstructure and quality of the CVD-grown film/coating. This portion of the work has resulted in five journal publications [1-5] and one conference presentation [6]. Selected results pertaining to this portion of the project are given in Appendix B.

List of All Publications and Technical Reports

Journal Publications

1. Grujicic, M., and Lai, S., "Atomistic Simulation of Chemical Vapor Deposition of (111)-oriented Diamond Film Using a Kinetic Monte Carlo Method," Journal of Materials Science, 34, 1999, pp. 7-20.

2. Grujicic, M., and Lai, S., "Grain-scale Modeling of Microstructure Evolution in CVD-grown Polycrystalline Diamond Films," Journal of Materials Synthesis and Processing, 2000, pp. 73-86.

3. Grujicic, M., and Lai, S., "Multi-length Scale Modeling of CVD of Diamond: Part I A Combined Reactor Scale/Atomic Scale Analysis," Journal of Materials Science, 35, 2000, pp. 5359-5369.

4. Grujicic, M., and Lai, S., "Multi-length Scale Modeling of CVD of Diamond: Part II A Combined Atomic Scale/Grain Scale Analysis," Journal of Materials Science, 35, 2000, pp. 5371-5381.

5. Grujicic, M. and Lai, S., "Multi-Length Scale Modeling of Chemical Vapor Deposition of Titanium Nitride Coatings", Journal of Materials Synthesis and Processing, 8, 2000, pp. 73-85.

Conference Presentations

1. Grujicic, M., Diefendorf, R.S. and Lai, S.G., "Multi-length scale Modeling of CVD of Diamond," International Conference on Carbon, Charleston, S.C., July 11-15, 1999.

List of All Participating Scientific Personnel Showing Any Advanced Degrees Earned by Them While Employed on the Project

Prof. Mica Grujicic	P.I.
Mr. Shugang Lai	Received PhD degree in May 2000

Bibliography

1. Grujicic, M., and Lai, S., "Atomistic Simulation of Chemical Vapor Deposition of (111)-oriented Diamond Film Using a Kinetic Monte Carlo Method," Journal of Materials Science, 34, 1999, pp. 7-20.

2. Grujicic, M., and Lai, S., "Grain-scale Modeling of Microstructure Evolution in CVD-grown Polycrystalline Diamond Films," Journal of Materials Synthesis and Processing, 2000, pp., 73-85.

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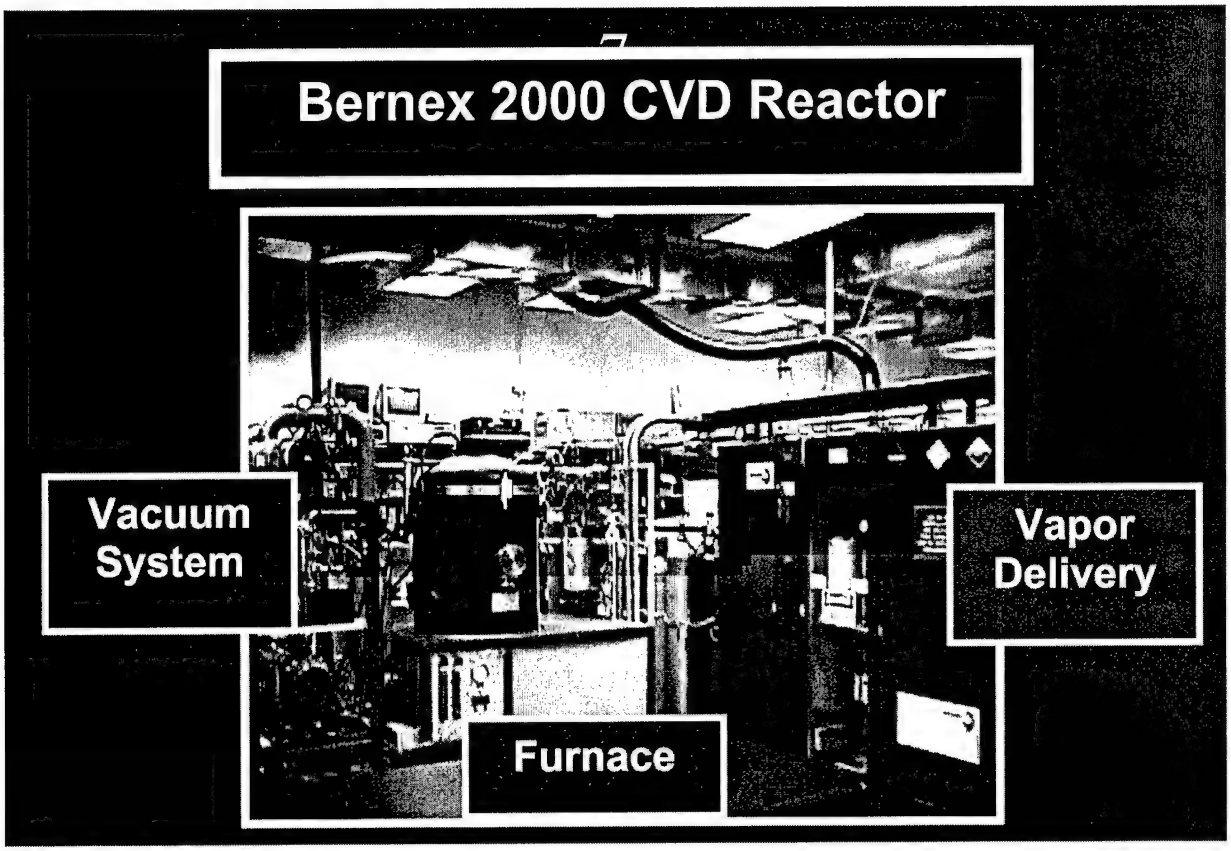
5. Grujicic, M. and Lai, S., "Multi-Length Scale Modeling of Chemical Vapor Deposition of Titanium Nitride Coatings," accepted for publication in Journal of Materials Science, 8, 2000, pp. 73-85.

6. Grujicic, M., Diefendorf, R.S. and Lai, S.G., "Multi-length scale Modeling of CVD of Diamond," International Conference on Carbon, Charleston, S.C., July 11-15, 1999.

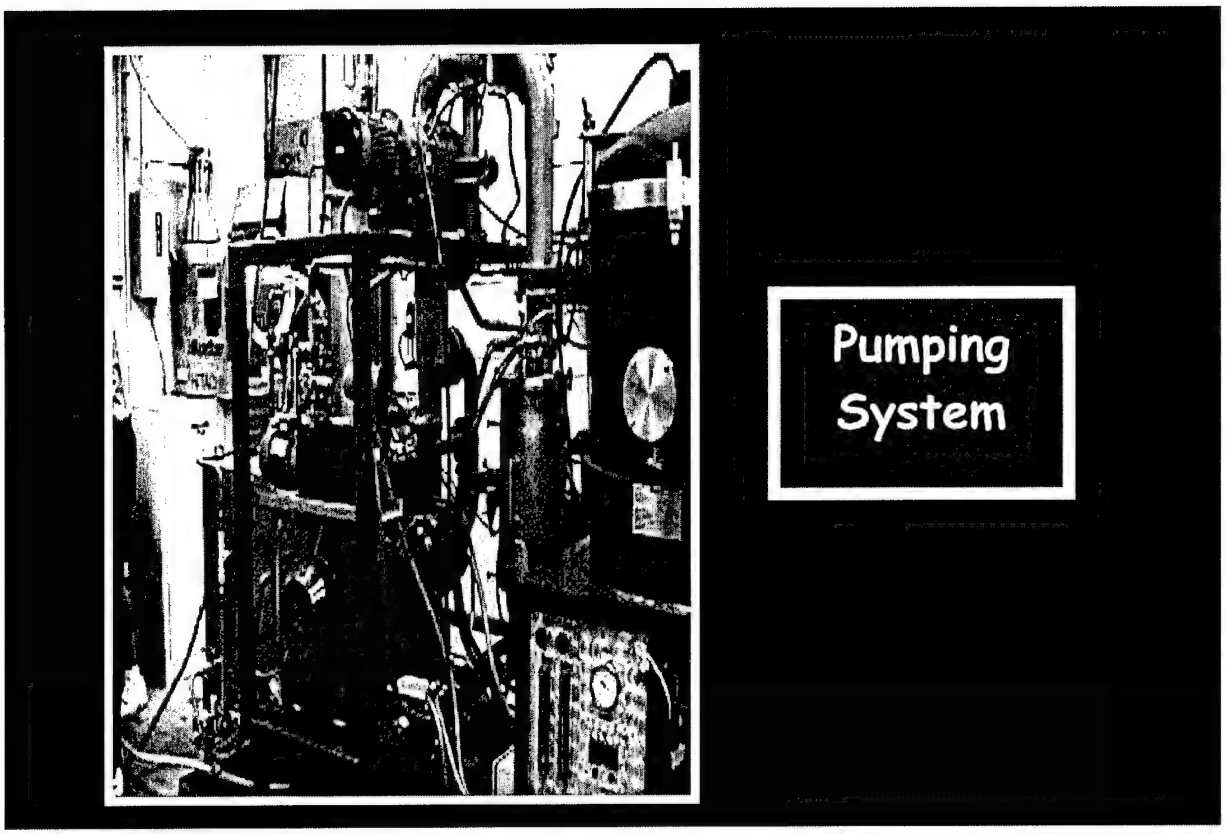
Appendix A

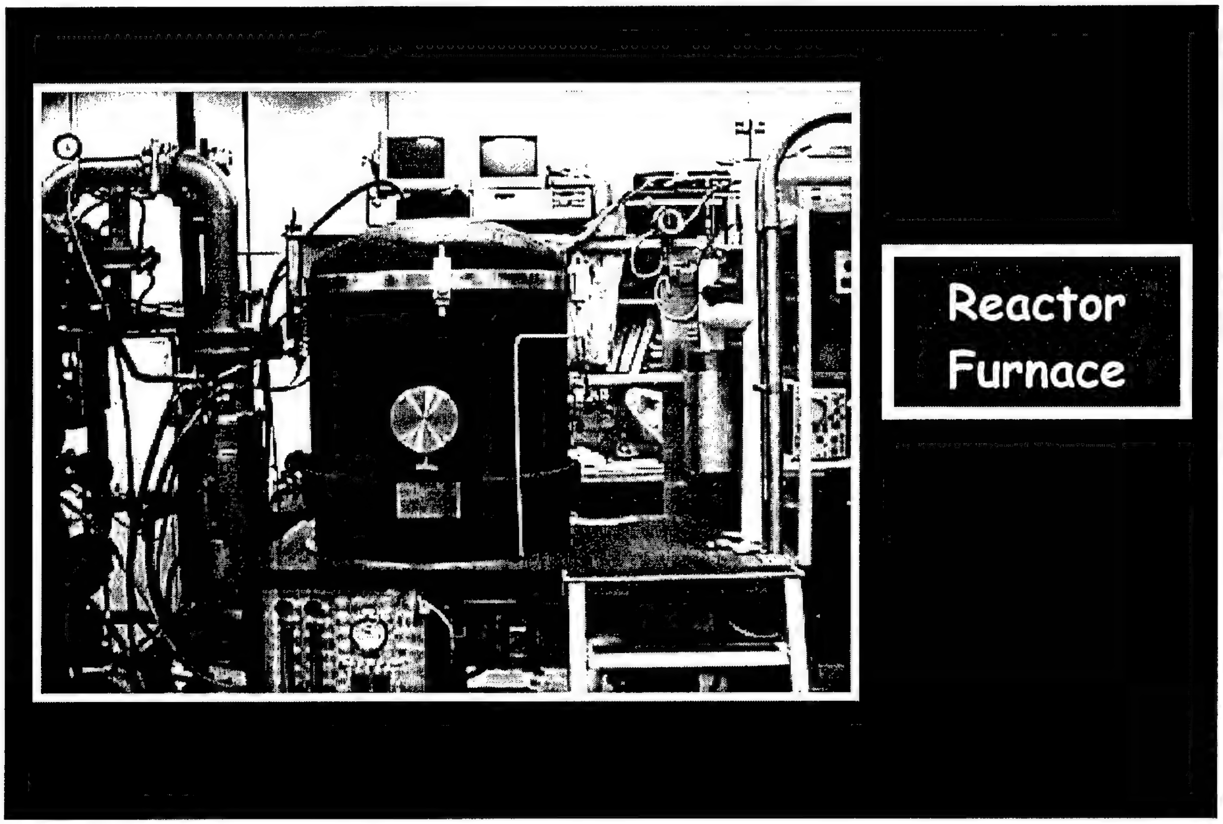
Bernex 2000

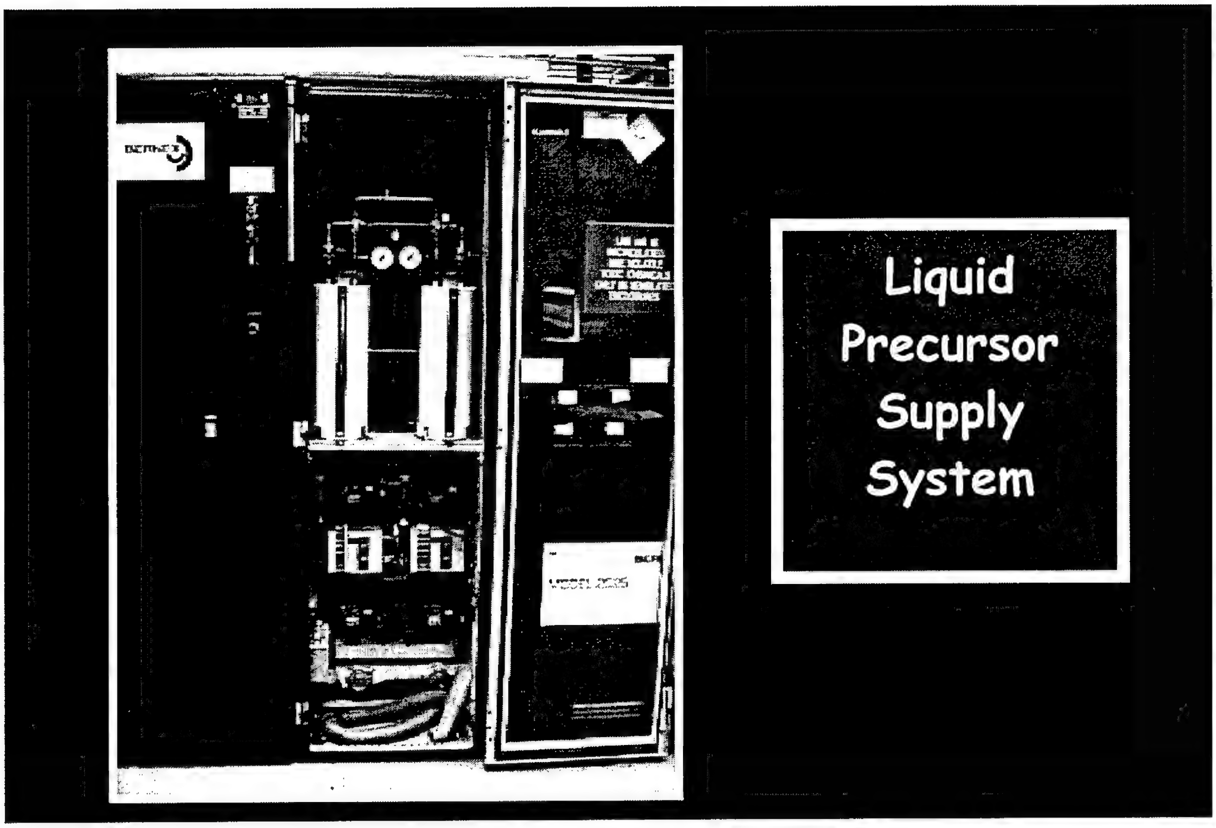
Large-scale Chemical Vapor Deposition Reactor

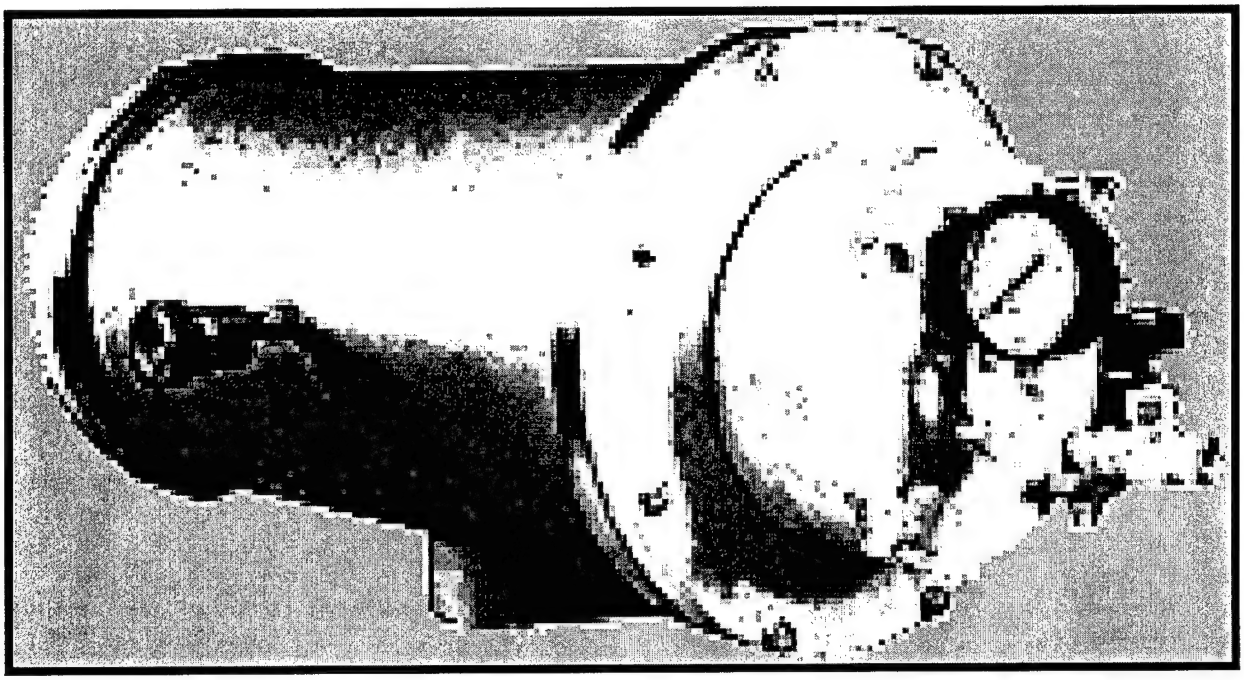

Bernex 2000 CVD Reactor
Vacuum System
Vapor Delivery
Furnace


Bernex
2000
CVD
Reactor


Pumping
System


Reactor
Furnace


Liquid
Precursor
Supply
System



Centorr Series 10
Graphite Tube Furnace

Appendix B

Multi-length Scale Modeling of Chemical Vapor Deposition Process

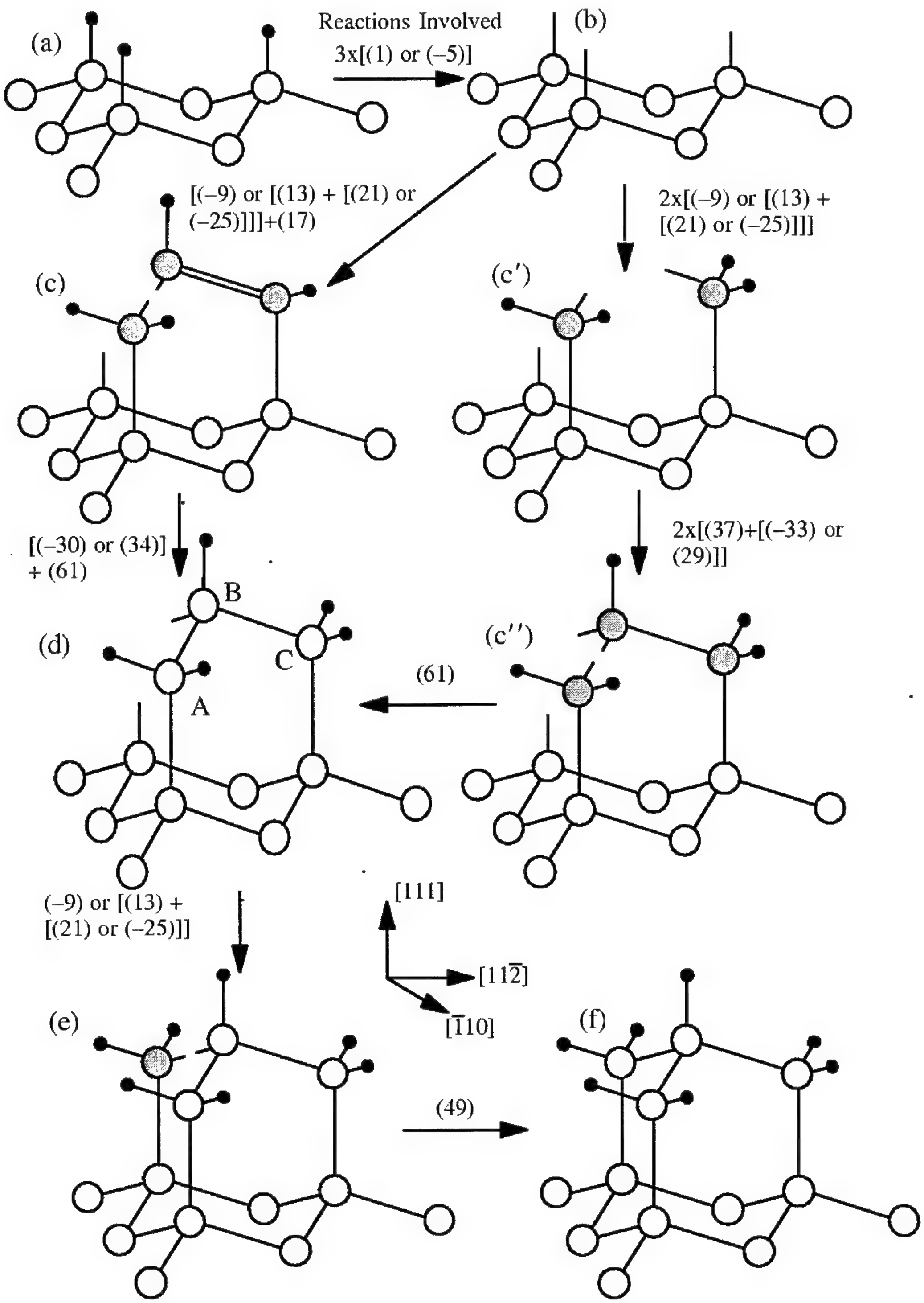


Figure 2. Sequence of steps involved in the nucleation of a new layer on an atomically flat (111) surface. Open circles represent diamond carbon atoms, shaded circles designate hydrocarbon carbon atoms, and small black circles stand for hydrogen atoms. Surface reactions (listed in Table I) involved in various steps of the process are given in parenthesis.

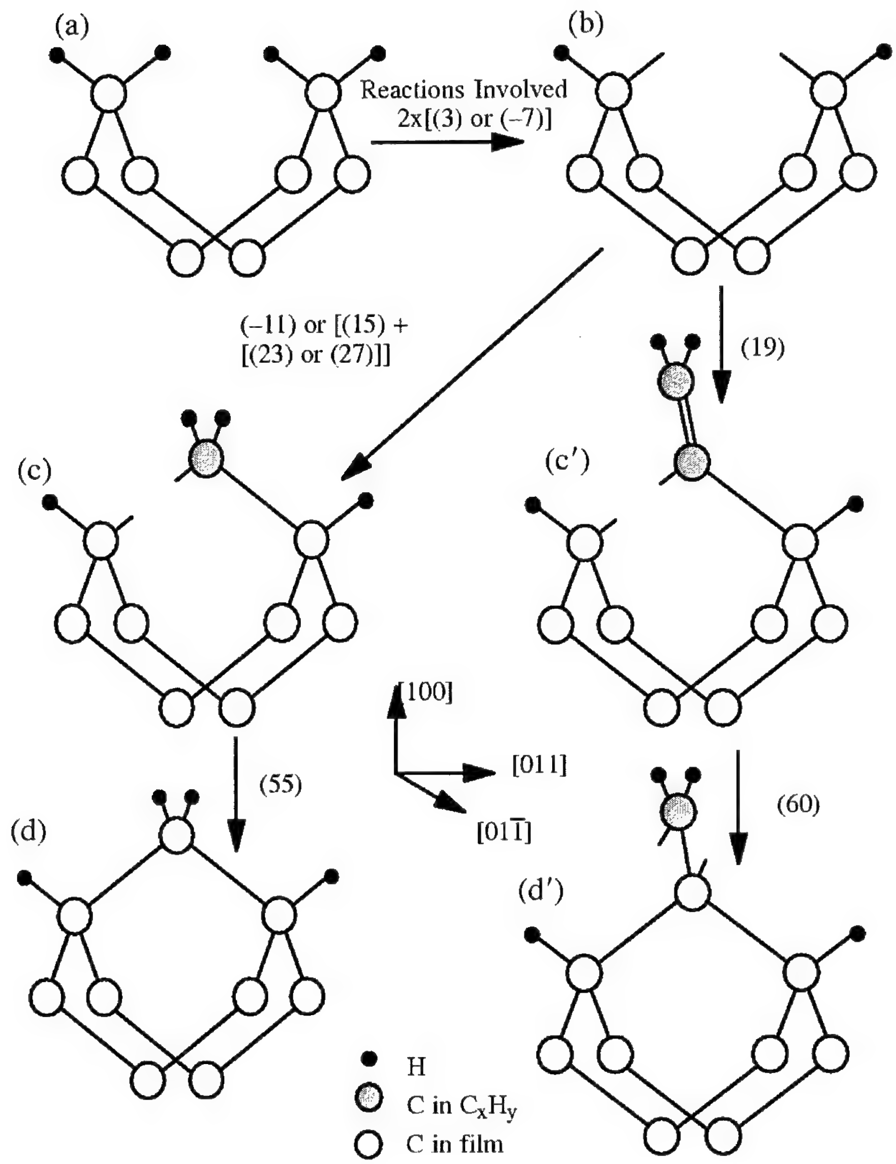


Figure 3. Growth of an (100)–oriented film by trough insertion mechanism. Open circles represent diamond carbon atoms, shaded circles designate hydrocarbon carbon atoms, and small black circles stand for hydrogen atoms. Surface reactions (listed in Table I) involved in various steps of the process are given in parenthesis.

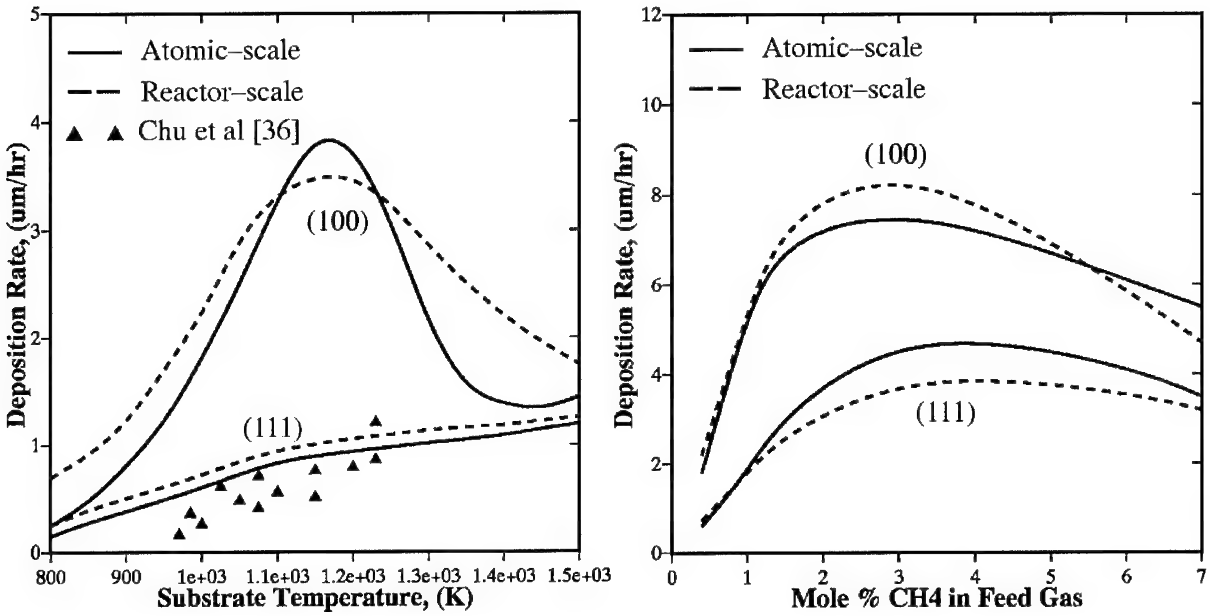


Figure 5. Reactor– and atomic scale analyses predicted (111)– and (100)–oriented film deposition rates as a function of (a) the substrate temperature and (b) concentration of CH_4 in feed gas. The remaining processing condition are as indicated in Figure 4.

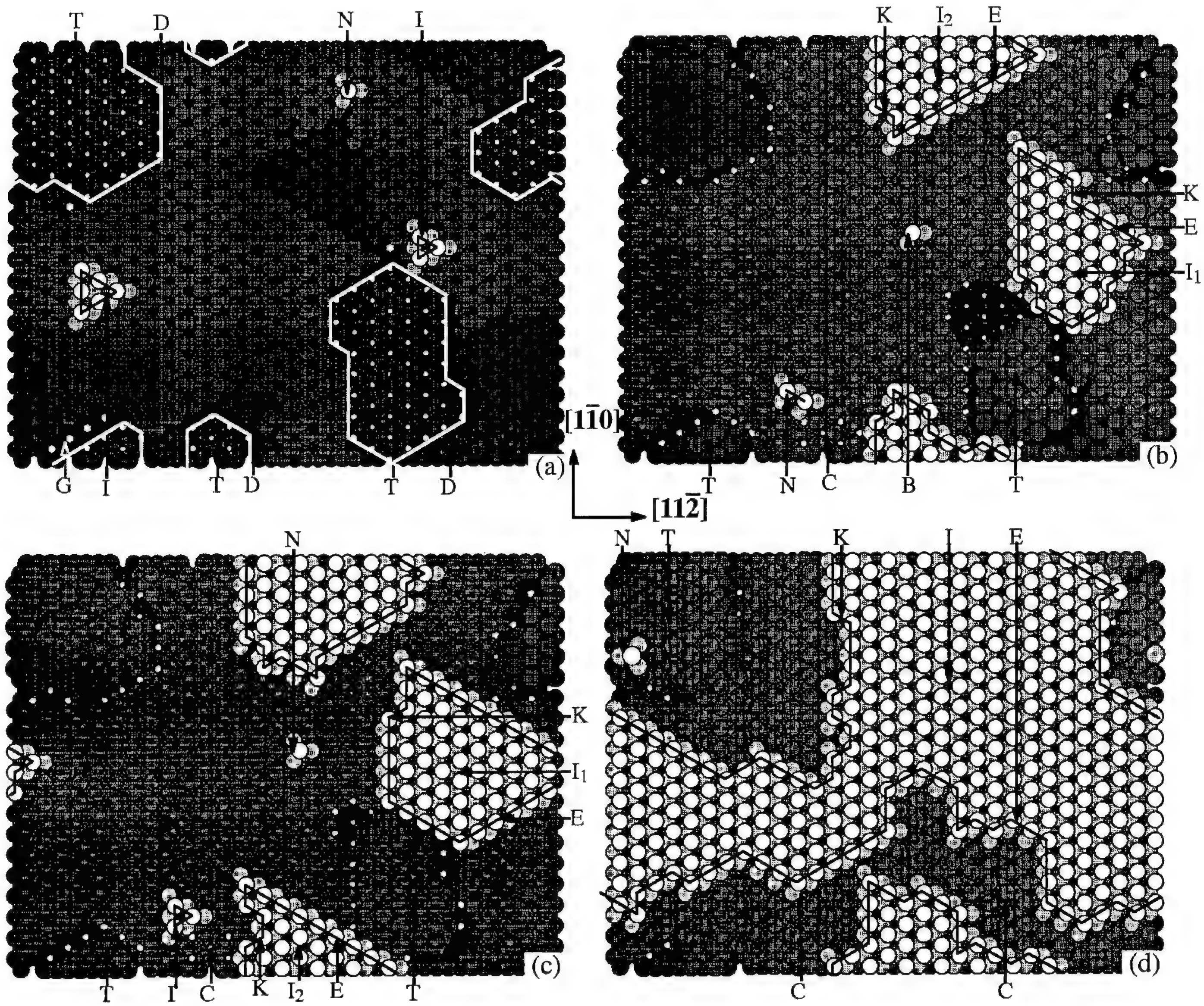


Figure 5. Top view of an (111)–oriented diamond film obtained under the following CVD conditions in the reactor: Reactive gas at the reactor inlet (0.4% CH_4, 92.5% H_2), T_{heator}= 2000 K, $T_{substrate}$= 1000 K, p= 20.25 Torr, Heater–to–Substrate Distance = 1.3cm. Deposition times: (a) 0.87s; (b) 1.81s; (c) 2.07s and (d) 2.85s. Nomenclature: B – 3–carbon bridge, C – Twin covered by regular crystal, D – Dislocation loop, E – Edge, G – Gap, I – Island, K – Kink, N – Nucleus, T – Twin, V – Void

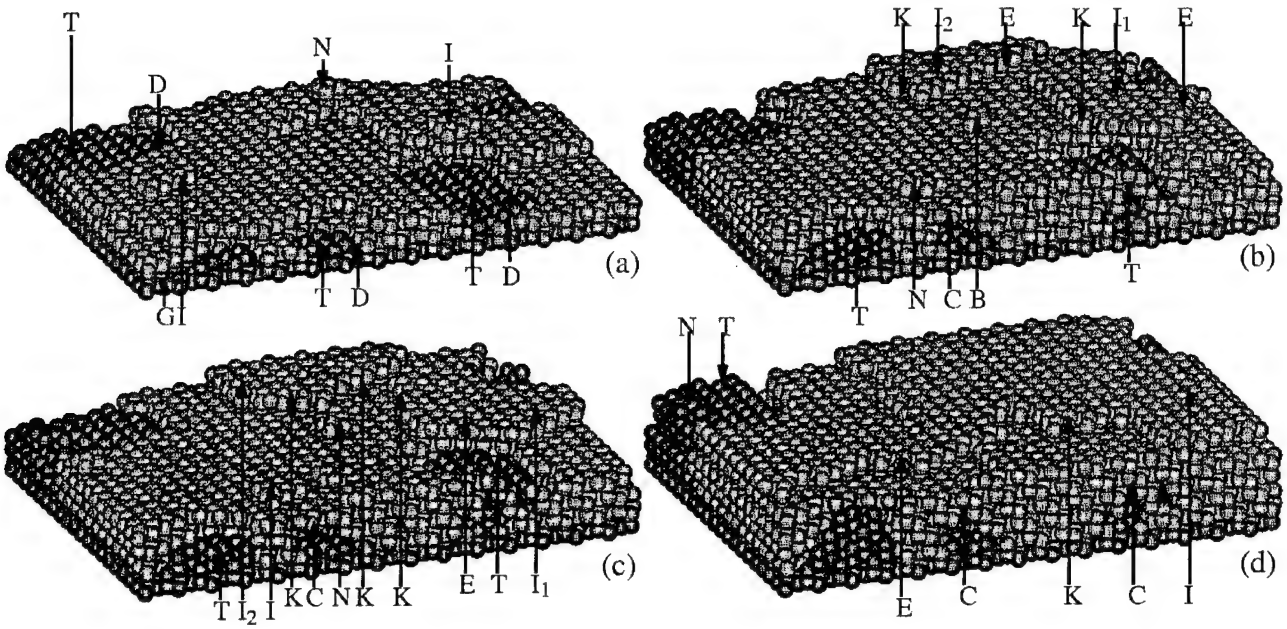


Figure 6. The side view of the four (111)–oriented diamond films shown in Figures 5(a)–(d).

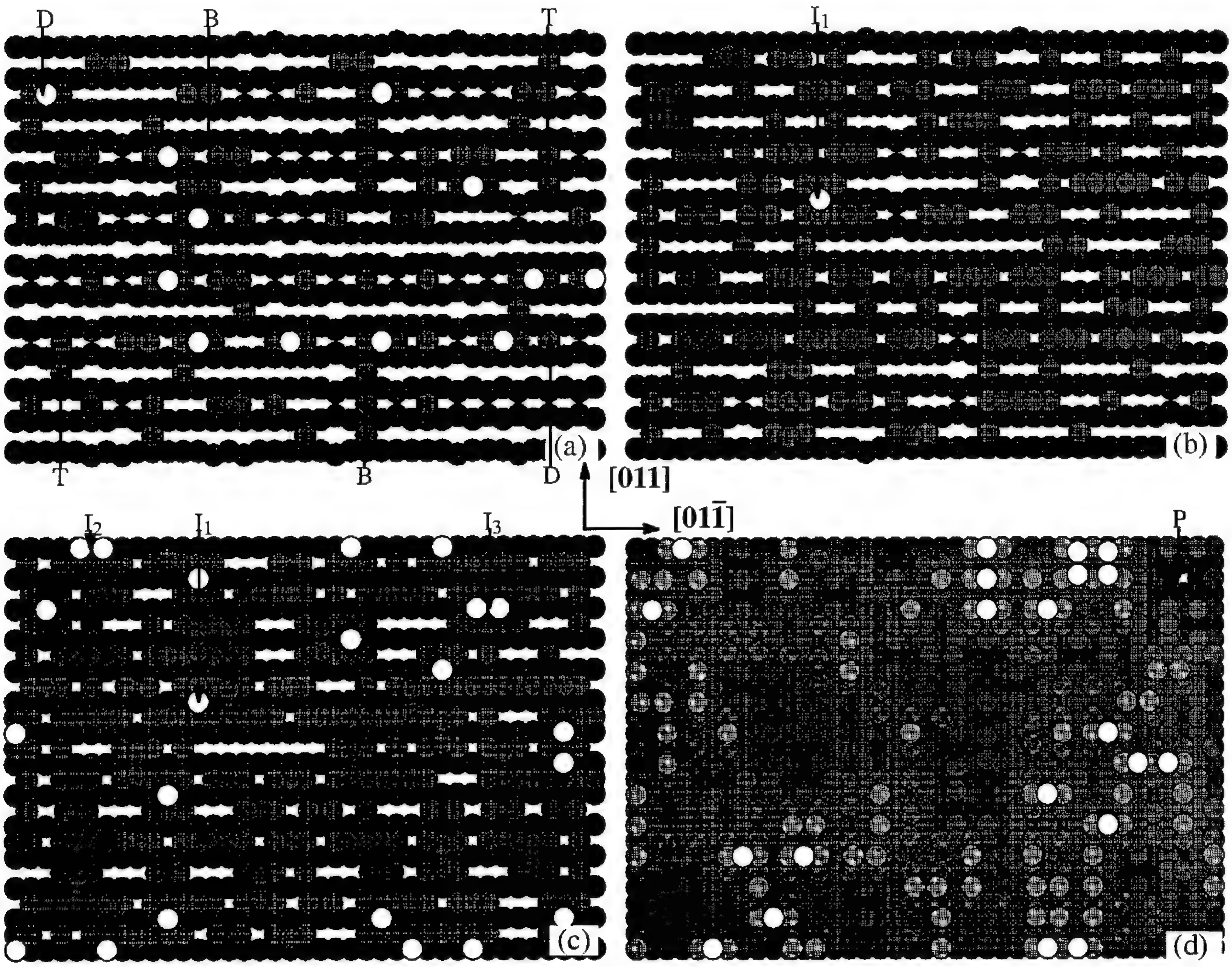


Figure 9. Top view of four (100) surface configurations obtained under the CVD conditions identical to the ones listed in Figure 5. Deposition times: (a) 0.01s; (b) 0.018s; (c) 0.032s and (d) 0.208s. Nomenclature: B—BCN mechanism, D—Dimer insertion mechanism, P—Pit, I—Island, T—Trough insertion mechanism.

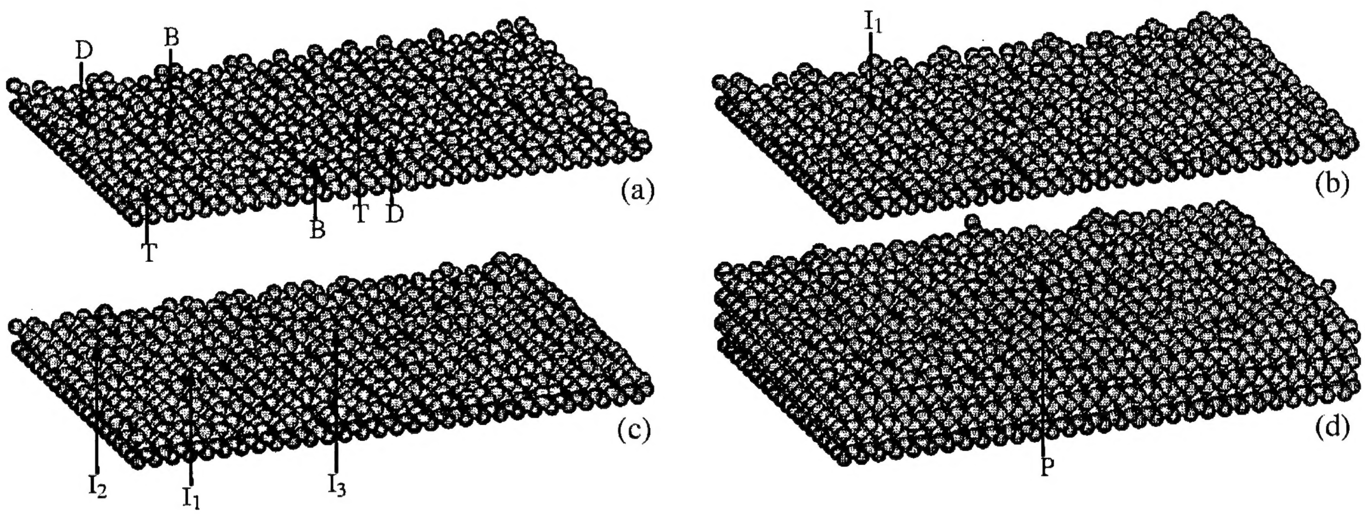


Figure 10. Side view of the four (100)–oriented diamond films shown in Figures 9(a)–(d).

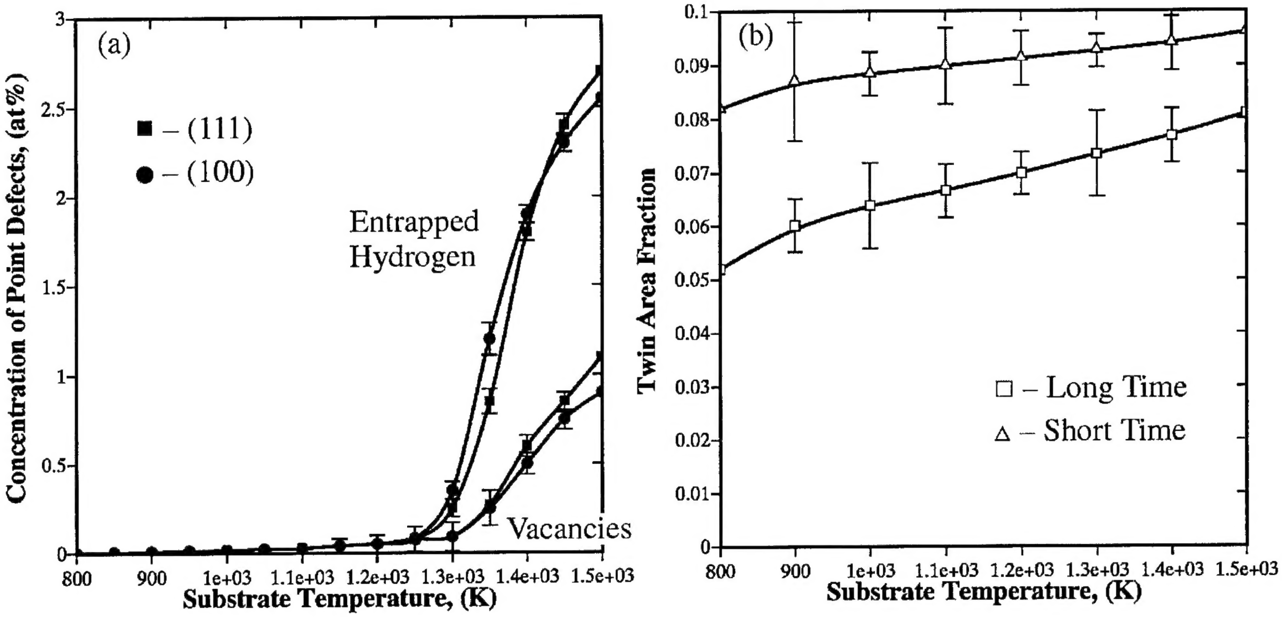


Figure 8. Effect of the substrate temperature on the concentration of vacancies and entrapped hydrogen atoms in (111)– and (100)–oriented diamond films, (a), and twins in (111)–oriented diamond films, (b), under the CVD conditions specified in Figure 5. Error bars represent on standard deviation over five simulation runs.

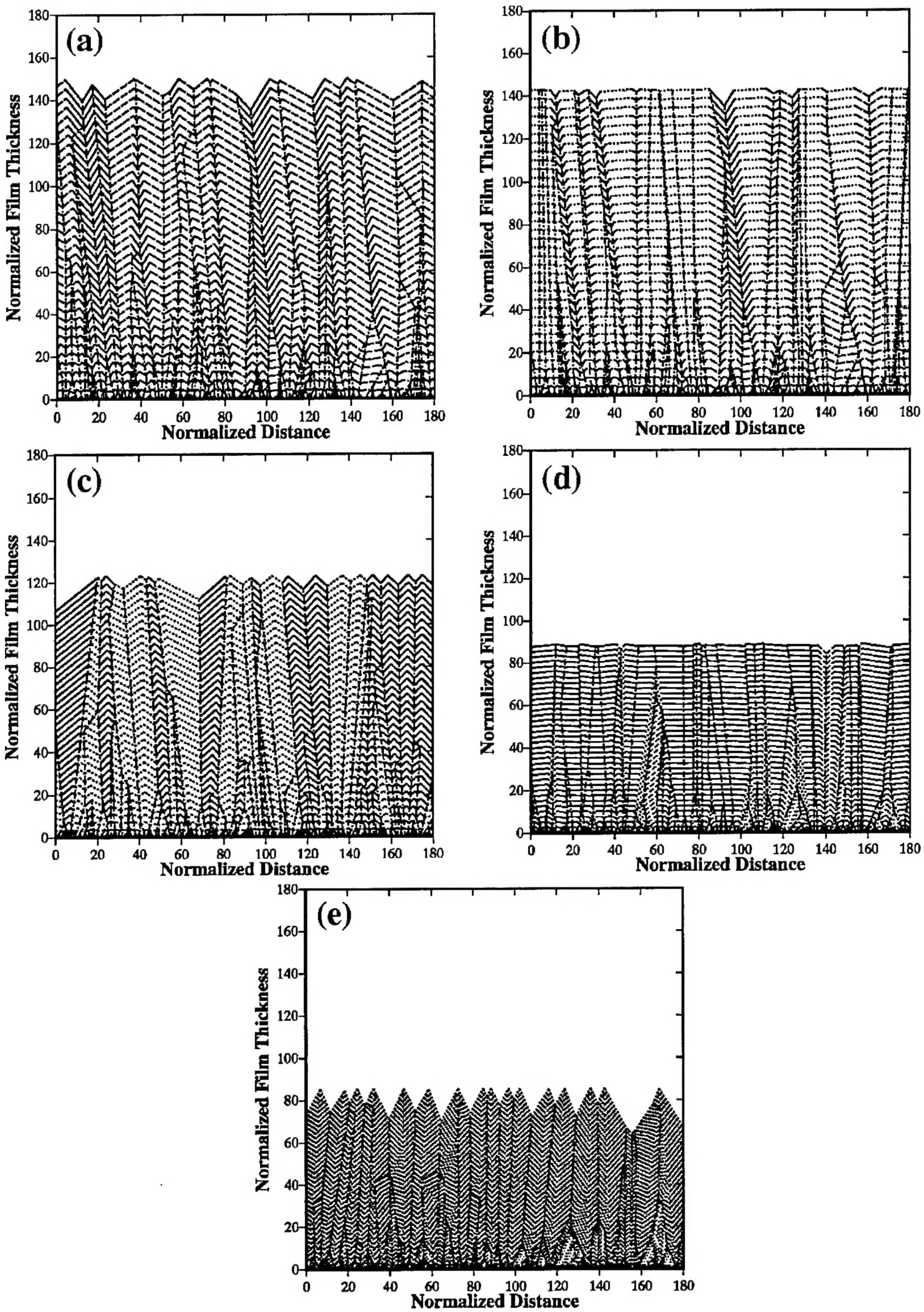


Figure 2. **The microstructure of polycrystalline diamond films deposited under the growth–rate parameter, α=: (a) 1.0; (b) 1.05; (c) 1.5; (d) 2.95 and (e) 3.0. Both the x– and y–axis are normalized with respect to the average nucleus spacing, d_0. The following line type nomenclature is used: dash–dot=grain boundaries, solid={100} facets, dotted ={111} facets, dashed = {100}/{100} facets, and three–dot space={111}/{111} facets.**

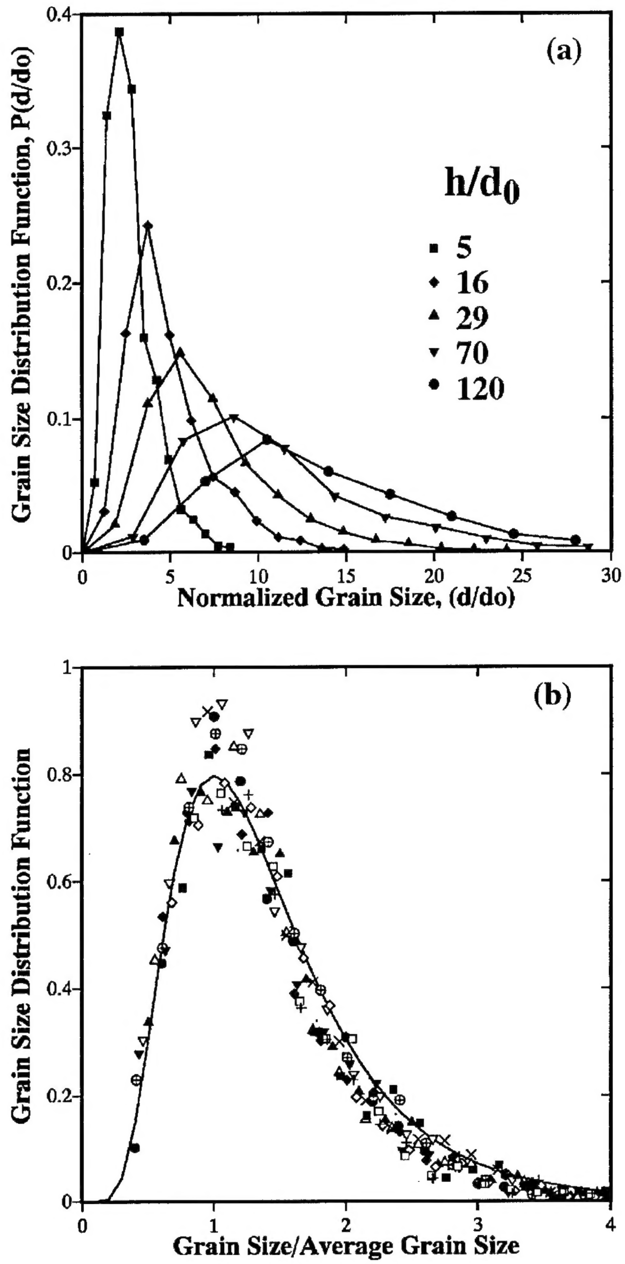


Figure 4. **(a) The distribution function for the grain size normalized with respect to the average nucleus spacing, d_0, at five film thicknesses for the growth–rate parameter α=1.5. (b) The distribution function for the grain size normalized with respect to the corresponding average grain size, $\bar{d}$, for five α values and three film thicknesses.**